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# A Dicopper Nitrenoid by Oxidation of a Cu<sup>I</sup>Cu<sup>I</sup> Core: Synthesis, Electronic Structure, and Reactivity

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**ABSTRACT:** A dicopper nitrenoid complex was prepared by formal oxidative addition of the nitrenoid fragment to a dicopper(I) center by reaction with the iminoiodinane PhINTs (Ts = tosylate). This nitrenoid complex, (DPFN)Cu<sub>2</sub>( $\mu$ -NTs)[NTf<sub>2</sub>]<sub>2</sub> (DPFN = 2,7-bis(fluorodi(2-pyridyl)methyl)-1,8-naphthyridine), is a powerful H atom abstractor that reacts with a range of strong C–H bonds to form a mixed-valence Cu(I)/Cu(II)  $\mu$ -NHTs amido complex in the first example of a clean H atom transfer to a dicopper nitrenoid core. In line with this reactivity, DFT calculations reveal that the nitrenoid is best described as an iminyl (NR radical anion) complex. The nitrenoid was trapped by the addition of water to form a mixed-donor hydroxo/amido dicopper(II) complex, which was independently obtained by reaction of a Cu<sub>2</sub>( $\mu$ -OH)<sub>2</sub> complex with an amine through a protonolysis pathway. This mixed-donor complex is an analogue for the proposed intermediate in copper-catalyzed Chan–Evans–Lam coupling, which proceeds via C–X (X = N or O) bond formation. Treatment of the dicopper(II) mixed donor complex with MgPh<sub>2</sub>(THF)<sub>2</sub> resulted in generation of a mixture that includes both phenol and a previously reported dicopper(I) bridging phenyl complex, illustrating that both reduction of dicopper(II) to dicopper(I) and concomitant C–X bond formation are feasible.

# INTRODUCTION

Given the importance of C-O and C-N bonds in natural products,<sup>1</sup> pharmaceuticals,<sup>2</sup> and organic materials,<sup>3</sup> the development of efficient and selective methods for their formation has been a rich field of study for many years.<sup>4-6</sup> Powerful synthetic methods for forming such bonds are based on a wide range of transition-metal-catalyzed reactions. In this context, Buchwald-Hartwig amination has emerged as a significant process which can be used to form a wide array of  $C(sp^2)$ -N bonds in selective fashion, typically by the coupling of an aryl halide with an amine in the presence of a palladium catalyst.7 An attractive alternative reaction is Chan-Evans-Lam coupling, a process that generates  $C(sp^2)-X$  bonds via the copper-catalyzed oxidative coupling of amines, alcohols, or thiols with boronic acids.<sup>8-11</sup> Although less frequently used than Buchwald-Hartwig amination, Chan-Evans-Lam coupling offers several advantages in that it features a more earthabundant metal, utilizes air as the terminal oxidant, and operates with simple amines, rather than costly phosphines, as effective ligands.

Aside from cross-coupling, common types of coppercatalyzed C–N bond forming processes include aziridination<sup>12</sup> and C–H amination,<sup>13,14</sup> both of which are thought to proceed by mechanisms involving copper nitrenoid intermediates. These key species tend to be highly reactive and usually result from reaction of a low-valent copper complex with N-based oxidants like organoazides and iminoiodinanes.<sup>15–18</sup> In 2012, Ray and co-workers demonstrated that interaction with scandium(III) stabilizes a copper tosylnitrenoid, which is metastable ( $t_{1/2} \sim 27$  min at -90 °C).<sup>19</sup> Subsequent work from the same group extended the scope of this chemistry to arylnitrenoids<sup>20</sup> and other Lewis acid stabilizers.<sup>21</sup> Although copper-catalyzed C–H amination was first reported in 1967 by Kwart and Khan,<sup>22</sup> it was only recently that Betley and co-

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workers published the first example of a well-defined, terminal copper nitrenoid species (Scheme 1, middle left).<sup>23</sup> Interest-

#### Scheme 1. Examples of Copper Nitrenoid Complexes Warren (2008)



ingly, X-ray absorption spectroscopy (XAS) experiments and density functional theory (DFT) calculations revealed that Betley's nitrenoid complex is best described as a triplet nitrene bound to a copper(I) metal center. Shortly thereafter, the same group reported the synthesis and detailed electronic structure of dicopper nitrenoid complexes tethered by a xanthene-based binucleating ligand (Scheme 1, middle right).<sup>24</sup> These complexes were reduced with KC<sub>8</sub> to yield the corresponding anionic nitrenoid complexes, which are surprisingly inert toward typical reactions like nitrene transfer and hydrogen atom transfer (HAT). The Warren group has made significant contributions to C–H amination catalysis,<sup>25</sup> demonstrating that oxidation of copper  $\beta$ -diketiminate (nacnac) complexes with organoazides can form dicopper nitrenoids<sup>26–29</sup> as the resting species (Scheme 1, top).

This laboratory explores structure, bonding, and reactivity in dicopper complexes of the 2,7-bis(fluoro-di(2-pyridyl)methyl)-1,8-naphthyridine (DPFN) ligand, which stabilizes dicopper units<sup>30,31</sup> featuring a range of bridging moieties.<sup>32–38</sup> Thus, this platform seemed well positioned to provide access to dicopper nitrenoid complexes. Herein, we report the synthesis, electronic structure, and reactivity of a dicopper nitrenoid complex that readily activates C–H bonds and adds water to form mixed O,N-donor dicopper(II) species. The latter undergo C–X (X = O or N) couplings when treated with diphenylmagnesium.

# RESULTS AND DISCUSSION

The complex  $(DPFN)Cu_2(\mu$ -NCMe) $[NTf_2]_2$  (1,  $NTf_2 = N(SO_2CF_3)_2)^{36}$  is a versatile starting material for a range of different transformations. Initial attempts to access dicopper nitrenoid complexes involved treatment of 1 with a variety of alkyl and aromatic azides (e.g., adamantyl azide, *p*-tolyl azide, and xylyl azide). However, these reactions yielded complex

mixtures of paramagnetic species that could not be separated (see the Supporting Information for details). In contrast, reaction of 1 with the hypervalent iodine reagent [N-(p-toluenesulfonyl)imino]phenyliodinane (PhINTs)<sup>39</sup> in THF resulted in an instant color change from orange-red to dark purple, followed by a second color change to dark green within seconds. A <sup>1</sup>H NMR analysis of the resulting mixture shows complete consumption of 1 and generation of an equivalent of iodobenzene as well as several broad peaks indicating formation of a paramagnetic species. The <sup>19</sup>F NMR spectrum contains a large resonance at -79.8 ppm due to the triflimide anion and a single broad resonance at -175.2 ppm for the DPFN ligand of a new (DPFN)Cu<sub>2</sub>-containing product.

X-ray quality crystals of the new product were grown by slow evaporation of an *o*-difluorobenzene (*o*-DFB)/toluene (1:1) solution, and diffraction studies identified the product as the amido complex (DPFN)Cu<sub>2</sub>( $\mu$ -NHTs)[NTf<sub>2</sub>]<sub>2</sub> (**2**; Scheme 2

Scheme 2. Synthesis of 2 via Oxidation of 1 (Isolated Yield in Parentheses)





**Figure 1.** Solid-state structure of **2** (50% probability ellipsoids). All hydrogens except that on the amido, as well as two  $NTf_2^-$  anions and solvent of crystallization, are omitted for clarity. The dashed line represents a cuprophilic interaction.

and Figure 1). The dark green product was isolated in high yield (88%) as an analytically pure powder by precipitation from THF solution with pentane. An infrared spectrum reveals a broad band at 3201 cm<sup>-1</sup> assigned to the amido N–H bond, and the Evans method provides an effective magnetic moment of  $\mu_{\text{eff}} = 1.8 \ \mu_{\text{B}}$ , consistent with an S = 1/2 system.

Given the previously observed variability in oxidation states for dicopper complexes with nitrogen-based ligands,<sup>32,33,40–44</sup> it was of interest to probe the electronic structure of complex **2** 

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by EPR spectroscopy. The X-band EPR spectra of frozen THF solutions of **2** were similar between 10 and 60 K, exhibiting rhombic signals with at least six discernible peaks at  $g \approx 2.0$  (Figure 2). Numerical simulation of the spectrum suggests inequivalent delocalization of the unpaired electron spin (S = 1/2) over both copper centers at these temperatures (10–60 K).<sup>22,33,45</sup>



**Figure 2.** Simulated (red) and experimental (black) EPR spectrum of 2 acquired at 10 K. The numerical simulation was obtained with *g* values of  $g_1 = 2.0363$ ,  $g_2 = 2.0923$ , and  $g_3 = 2.2433$  and principal hyperfine components of  $[A_1^{\text{Cul}} = 34, A_2^{\text{Cul}} = 45, A_3^{\text{Cul}} = 90.64] \times 10^{-4} \text{ T}$  and  $[A_1^{\text{Cu2}} = 7, A_2^{\text{Cu2}} = 15, A_3^{\text{Cu2}} = 59.67] \times 10^{-4} \text{ T}$ .

Cyclic voltammetry of **2** reveals a single reversible reduction feature ( $E^{\circ} = +0.070$  V vs  $[Cp_2Fe]^{0/+}$ ; see the Supporting Information), which occurs between separate, irreversible reduction and oxidation events. This reversible feature is similar to those observed for the mixed valence phenyl<sup>32</sup> and alkynyl<sup>33</sup> complexes previously reported. To determine whether the corresponding dicopper(I) amido complex is accessible, **2** was treated with KC<sub>8</sub> at room temperature in THF. Upon mixing, the green color of the supernatant quickly changed to red-brown, and the <sup>1</sup>H NMR spectrum indicates formation of a new diamagnetic product, assigned as  $[(DPFN)Cu_2(\mu-NHTs)][NTf_2]$  (**3**). Conveniently, **3** was also prepared via an independent salt metathesis route from reaction of **1** with LiNHTs (see Scheme 3).

Vapor diffusion of cold (-30 °C) Et<sub>2</sub>O onto a concentrated solution of 3 in THF over 2 days resulted in the growth of brown, X-ray quality crystals, and the solid-state structure of 3 was determined by single-crystal diffraction analysis (Figure 3). The structure of 3 resembles that of the pentafluorophenolate

# Scheme 3. Synthesis of 3 via Salt Metathesis (Isolated Yield in Parentheses)





**Figure 3.** Solid-state structure of 3 (50% probability ellipsoids). All hydrogens except that on the amido as well as an  $NTf_2^-$  anion and solvent of crystallization are omitted for clarity. The dashed line represents a cuprophilic interaction.

complex [(DPFN)Cu<sub>2</sub>( $\mu$ -OC<sub>6</sub>F<sub>5</sub>)][NTf<sub>2</sub>] recently reported by our group.<sup>35</sup> The most notable feature of the solid-state structure of **3** is the remarkably elongated Cu···Cu distance of 2.6652(5) Å (for comparison, the Cu···Cu distance in **2** is 2.386(1) Å). Moreover, the Cu1–N7 and Cu2–N7 bonds in **3** are identical within experimental error and are also lengthened by ~0.05 Å with respect to comparable distances in **2**. This symmetrical elongation is in contrast to the asymmetric structural changes observed in the phenyl<sup>32</sup> and alkynyl<sup>33</sup> analogues of **2**, which both feature tilting of the bridging ligands upon oxidation of dicopper(I) to mixed valence Cu(I)/ Cu(II) due to significant contraction of one Cu–C bond relative to the other.

The purple intermediate observed during the oxidation of 1 with PhINTs would appear to correspond to the nitrenoid complex  $[(DPFN)Cu_2(\mu-NTs)][NTf_2]_2$  (4, Scheme 4), which could react via a hydrogen atom transfer (HAT) reaction to give compound 2 (with the THF solvent as a likely H atom source). HAT is an important fundamental reaction<sup>46</sup> that has been characterized for a range of C–H functionalization processes, including C–H oxygenation by cytochrome P450 enzymes<sup>47,48</sup> and C–H amination by metal nitrenoids,<sup>49</sup> and

Scheme 4. Synthesis of 5 and Oxidation to 4: <sup>a</sup>Isolated Yield in Parentheses; <sup>b</sup>Based on <sup>19</sup>F NMR Spectroscopy



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has been probed experimentally for dicopper oxo complexes.<sup>41</sup> Although monocopper nitrenoids have been found to undergo HAT with formation of copper amido complexes,<sup>16,19</sup> to the best of our knowledge this is the first example of a clean HAT process occurring at a dicopper nitrenoid complex. In an attempt to suppress this HAT process, we treated 1 with PhINTs in *o*-DFB, which has much stronger C–H bonds compared to those of THF.<sup>50</sup> A color change from purple to dark green was again observed (although over the course of minutes rather than seconds), suggesting that the putative nitrenoid complex 4 readily abstracts H atoms from a component of the reaction mixture.

Because the acetonitrile ligand in 1 is a potential source of H atoms, an alternate starting material bearing a bridging L-type ligand without reactive C–H bonds was sought. Carbon monoxide has been shown to bind to dicopper cores supported by the related 2,7-bis(1,1-dipyridylethyl)-1,8-naphthyridine (DPEN) ligand,<sup>51</sup> and an analogous DPFN complex was prepared by stirring 1 under an atmosphere of CO to give  $[(DPFN)Cu_2(\mu-CO)][NTf_2]_2$  (5) in 95% isolated yield as an off-white powder (Scheme 4).

Recrystallization of 5 from cold  $(-30 \ ^{\circ}\text{C})$  THF afforded Xray quality crystals, and the solid-state structure is shown in Figure 4. Compound 5 is structurally similar to the DPEN analogue reported previously.<sup>51</sup>



**Figure 4.** Solid-state structure of **5** (50% probability ellipsoids). All hydrogens as well as two  $NTf_2^-$  anions and solvent of crystallization are omitted for clarity. The dashed line represents a cuprophilic interaction.

Interestingly, reaction of **5** with PhINTs in *o*-DFB resulted in formation of a purple solution of **4** that persisted for days at -30 °C. A <sup>1</sup>H NMR analysis of the purple solution demonstrates that **4** also displays broad, paramagnetically shifted resonances, and <sup>19</sup>F NMR spectroscopy shows quantitative conversion of **5** and concomitant formation of a new, broad DPFN resonance at -173.5 ppm. An Evans method measurement reveals a  $\mu_{eff}$  value of 2.7  $\mu_{B}$ , consistent with two strongly coupled copper(II) centers.<sup>43</sup> This triplet ground state is distinct from the examples of dicopper nitrenoid complexes reported by Betley<sup>24</sup> and Warren,<sup>26,27</sup> all of which are diamagnetic and feature either aliphatic or aromatic substituents on the nitrenoid moiety. Corona et al. have recently reported a monomeric copper nitrenoid species with a triplet ground state.<sup>15</sup> It is noteworthy that Cundari and co-workers have reported a computational study that found that heteroatom substituents on nickel nitrenoid moieties result in stabilization of the triplet state versus the singlet state.<sup>52</sup> This is in contrast to examples where the nitrenoid moiety bears aliphatic or aromatic substituents, in which case the singlet configuration is favored.<sup>53,54</sup>

Although compound 4 was readily generated *in situ* by using the above method, it was difficult to isolate as attempts to precipitate 4 from *o*-DFB by the addition of  $Et_2O$  or pentane resulted in formation of an intractable purple tar. Many attempts to grow single crystals of 4 were unsuccessful, typically resulting in green crystals of the amido complex 2 instead. Thus, DFT computational methods (BP86/def2-TZVPP/SMD-MeCN) were used to gain additional insight into the unusual electronic structure of 4. The dicationic portion of 4 exhibits both singlet (closed and open shell) and triplet states as well as several coordination modes for the  $\mu$ -NTs ligand. The crystal structure of 2—after removal of the amide hydrogen—was used as a starting point for DFT geometry optimizations (Figure 5, top). Calculations suggest



**Figure 5.** DFT calculated geometry (top) and spin density plot (bottom) of dicationic dicopper nitrenoid complex 4, triplet ground state.

that the triplet spin state is more stable ( $\Delta G$ ) than the openshell singlet by 5.8 kcal/mol. Löwdin population analysis<sup>55</sup> of the spin densities for the calculated triplet ground state of 4 reveals ~0.4 unpaired e<sup>-</sup> on each Cu with 0.6 e<sup>-</sup> of spin density on the N of the bridging NTs (see Figure 5, bottom). The remaining spin density is diffused over the ligating nitrogen atoms of the supporting DPFN ligand and the oxygen atoms of the tosylate group. The spin density on both the nitrene nitrogen and the Cu suggests a ground state for 4 with

significant mixing of Cu(I)/Cu(II)character as well as significant iminyl (NR<sup>•-</sup>) character.<sup>56-58</sup>

The observed ability of 4 to abstract H atoms from both THF  $(C-H BDE \sim 92 \text{ kcal/mol})^{50}$  and acetonitrile (C-HBDE ~ 97 kcal/mol)<sup>50</sup> is remarkable given the paucity of analogous reactivity from the few known examples of dicopper nitrenoid complexes.<sup>24,26</sup> Notably, DFT calculations indicate the N-H BDE of complex 2 is  $97 \pm 3$  kcal/mol. Given this proclivity of 4 toward HAT, it was of interest to examine whether the bond dissociation free energy (BDFE) of the N– H bond of 2 could be determined.<sup>41,59</sup> Unfortunately, 4 reacts rapidly with the supporting electrolytes NBu<sub>4</sub>[NTf<sub>2</sub>] and PPN[Cl] (PPN = bis(triphenylphosphine)iminium), thwarting attempts to perform electrochemical analysis. Surprisingly, complex 4 proved to be poor at typical reactions of copper nitrenoids, such as styrene aziridination, C-H amination, and nitrene transfer (see the Supporting Information for details). Moreover, 4 decomposed to a complex mixture upon treatment with HNTf<sub>2</sub> in o-DFB. However, when compound 5 was exposed to PhINTs in the presence of a slight excess of water in dichloromethane (DCM) at -40 °C, a gradual color change from pale yellow to blue was observed. After filtration, the new product (DPFN)Cu<sub>2</sub>( $\mu$ -OH)( $\mu$ -NHTs)[NTf<sub>2</sub>]<sub>2</sub> (6, Scheme 5) was isolated following precipitation with Et<sub>2</sub>O.

Scheme 5. Synthesis of 6 via Apparent Trapping of 4 with Water (Isolated Yield in Parentheses)



Although the reaction of water with copper nitrenoids has recently been inferred,  $^{60,61}$  to the best of our knowledge this is the first well-defined example of this transformation.

Blue X-ray quality crystals of **6** were obtained by vapor diffusion of Et<sub>2</sub>O onto a concentrated THF solution at ambient temperature. The molecular structure corresponds to a dicopper(II) mixed donor hydroxo/amido species, with both anionic ligands bridging the two copper centers in a butterflytype structure (Figure 6). The related, symmetrical bis-(hydroxo) complex (DPFN)Cu<sub>2</sub>( $\mu$ -OH)<sub>2</sub>[NTf<sub>2</sub>]<sub>2</sub> (7), prepared via oxidation of **1** with air, was recently reported by our laboratory.<sup>37</sup> Interestingly, the elimination of water from complex **6** to regenerate **4** was not observed, even upon heating for extended periods (5 days at 80 °C) in *o*-DFB in the presence of molecular sieves, and **6** remained unchanged under these conditions.

An alternate synthetic route to compound **6** was achieved by treating 7 with  $H_2NTs$ , although this protonolysis reaction required the addition of molecular sieves for complete conversion (see the Supporting Information for details). Conveniently, it was found that other acidic substrates are suitable precursors for related protonolysis reactions. On addition of formic acid<sup>37</sup> or 2-hydroxypyridine<sup>62,63</sup> to 7, a rapid color change from deep blue to light blue or green, respectively, was observed. Both new products (**8** and **9**, Scheme **6**) were isolated as powders by simple precipitation with pentane and washing with Et<sub>2</sub>O. These results highlight



**Figure 6.** Solid-state structure of **6** (50% probability ellipsoids). All hydrogens except those on the amido and hydroxo ligands as well as two  $NTf_2^-$  anions and solvent of crystallization are omitted for clarity.

Scheme 6. Syntheses of 8 and 9 via Protonolysis (Isolated Yields in Parentheses)



the utility of protonolysis as an attractive synthetic route to mixed-donor dicopper(II) complexes with greater structural diversity than can be easily achieved via the previously described oxidation/ $H_2O$  addition protocol. Indeed, the iminoiodinanes used for the latter are usually limited to *N*-sulfonyl substituents.<sup>64</sup>

Dark blue X-ray quality crystals of **8** were grown by vapor diffusion of cold  $(-30 \ ^{\circ}C)$  Et<sub>2</sub>O onto a solution of **8** in THF (see Figure 7). In contrast to the structures of **6** and 7, which feature both anionic ligands bridging the two coppers in a symmetric fashion, the chelating formate of **8** is essentially *trans* to the naphthyridine core.

X-ray quality crystals of 9, grown in a similar manner, resulted in determination of the molecular structure shown in Figure 8. The structure of 9 is generally similar to that of 8, with the chelating pyridonate moiety bound almost directly across from the naphthyridine core of the DPFN ligand. This structural feature is accompanied by positioning of the hydroxyo group into the approximate plane defined by the four pyridyl nitrogens of the DPFN ligand. Interestingly, a second protonolysis event was not observed for either 8 or 9, as these were the only products formed even upon addition of an excess (up to 3 equiv) of the acidic substrate and molecular sieves to complex 7 over the course of days at room temperature.



**Figure 7.** Solid-state structure of **8** (50% probability ellipsoids). All hydrogens except those on the hydroxo and formate ligands, as well as two  $NTf_2^-$  anions and solvent of crystallization, are omitted for clarity.



Figure 8. Solid-state structure of 9 (50% probability ellipsoids). All hydrogens except that on the hydroxo, as well as two  $NTf_2^-$  anions and solvent of crystallization, are omitted for clarity.

These mixed donor dicopper(II) complexes, especially 6, bear a strong resemblance to proposed intermediates in the mechanism of Chan-Evans-Lam coupling.<sup>8-11</sup> Indeed, 6 is the first crystallographically characterized dicopper complex to feature both amido and hydroxo/alkoxo groups not tethered to the ancillary ligand. Thus, it seemed that 6 could provide an interesting model for gaining insights into Chan-Evans-Lam reactivity for a discrete dicopper system. In particular, both Xtype donor ligands could potentially undergo transmetalation with a traditional aryl organometallic reagent (such as boronic acids or harsher reagents like Grignards), which could then undergo C-X reductive elimination to produce an arylated amine or alcohol.<sup>65</sup> Initial attempts to induce this reactivity using traditional boron-based Chan-Evans-Lam coupling partners (i.e., PhB(OH)<sub>2</sub>, PhBcat (cat = catecholato), and PhBpin (pin = pinacolato)) resulted in complex mixtures of multiple products. The addition of a variety of bases, which have been shown to promote this reactivity in related systems,<sup>7,8</sup> instead resulted in the rapid consumption of 6 without improvement in desired product formation (see the Supporting Information).

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In contrast, addition of an excess (2 equiv) of MgPh<sub>2</sub>(THF)<sub>2</sub> to a solution of **6** resulted in an immediate color change from blue to red, followed by a subsequent change to dark green within minutes. The reaction mixture also developed a fine precipitate. By <sup>1</sup>H and <sup>19</sup>F NMR spectros-copy, the major DPFN-containing product in the reaction mixture was (DPFN)Cu<sub>2</sub>( $\mu$ -Ph)[NTf<sub>2</sub>] (**10**)<sup>32</sup> (71% <sup>1</sup>H NMR spectroscopic yield relative to **6**; Scheme 7). This demon-





strates successful reduction of the dicopper(II) core of 6 to dicopper(I). Significant amounts of biphenyl (Ph-Ph, 36%) were also detected in the reaction mixture by <sup>1</sup>H NMR spectroscopy. Notably, copper(II) has previously been shown to engage in related Grignard homocoupling processes.<sup>66-69</sup> The reaction mixture also contained benzene (1.1 equiv relative to complex 6), likely formed via a competing deprotonation pathway of either the OH or NHTs moieties of 6 by the Grignard reagent. To investigate the insoluble residue as magnesium salts of the coupled products, water (150 equiv) was added to the reaction mixture, and a subsequent <sup>1</sup>H NMR analysis reveals formation of phenol (PhOH, 48% yield) and free amine  $H_2NTs$  (64% yield) as the main new organic species, along with trace amounts (4% yield) of the C-N coupling product PhNHTs. This demonstrates that for this particular system C-O coupling is favored over C-N coupling. Phenol has previously been observed after treatment of phenyl organometallic reagents with a variety of O-based oxidants.

While the current data do not allow us to discern a mechanism for the C–X couplings, note that when these reactions also occurred in the presence of the radical scavengers 9,10-dihydroanthracene and "Bu<sub>3</sub>SnH, product formation was not affected. Thus, an inner-sphere (metal-based) coupling process may be more likely than an outer-sphere (radical-based) process (see the Supporting Information). Overall, these results demonstrate the feasibility of C–X coupling from dicopper(II) at a (DPFN)Cu<sub>2</sub> core, with formation of arylated organic products and regeneration of a dicopper(I) species. Efforts to induce catalytic turnover with these dicopper(II) systems are currently in progress.

# CONCLUSIONS

Copper nitrenoids are often proposed as reactive intermediates in C–N bond forming processes but have only recently been experimentally observed. In this contribution, we described the synthesis of a triplet dicopper nitrenoid that is very reactive, abstracting H atoms from a variety of strong C–H bonds to form a mixed-valence Cu(I)/Cu(II) amido complex. This

reactivity is in line with electronic structure calculations showing that the dicopper nitrenoid is best described as an iminyl radical fragment coupled to a mixed-valence Cu(I)/Cu(II) core. Although this nitrenoid complex performs poorly in traditional reactions like alkene aziridination and C–H amination, it can be trapped by the addition of water to form a mixed donor dicopper(II) complex in the first well-defined example of such a process. Finally, reactivity studies show that the mixed donor dicopper(II) complex can serve as an intermediate in C–O and C–N bond-forming reactions.

Overall, this work demonstrates that the (DPFN)Cu<sub>2</sub> scaffold is effective for stabilizing high-valent nitrenoids, engendering unusual reactivity that is distinct from previously described examples. It also highlights the use of a rigid, binucleating ligand scaffold to dramatically alter the chemistry of reactive moieties like nitrenoids, offering reaction pathways that may be of use in designing avenues for new bond-forming catalysis. It is hoped that this nitrenoid system will also point the way to the generation of other high valent dicopper fragments of interest, for example, an oxo ligand in the intriguing  $[Cu_2(\mu-O)]$  moiety of microporous materials<sup>74</sup> and enzymes,7 which has attracted considerable attention in the context of difficult C-H bond activations. These results should also contribute to development of new oxidative coupling processes using benign oxidants like air or iminoiodinanes, and multimetallic complexes as catalysts.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c02235.

Detailed experimental and computational methods (PDF)

#### **Accession Codes**

CCDC 2034513–2034519 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

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